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(54) **A method of forming an epitaxial layer of silicon**

(57) A method of forming an epitaxial layer of silicon on a surface of a monocrystalline silicon body is described in which a stream of hydrogen gas is passed over the body and, prior to passing a silicon-containing gas over the body to commence growth of the epitaxial layer, the surface of the body is cleaned by passing a fluorine-containing gas over the body with the stream of hydrogen gas and the body is then heated to the temperature at which the epitaxial layer is to be grown.

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Fig.1.

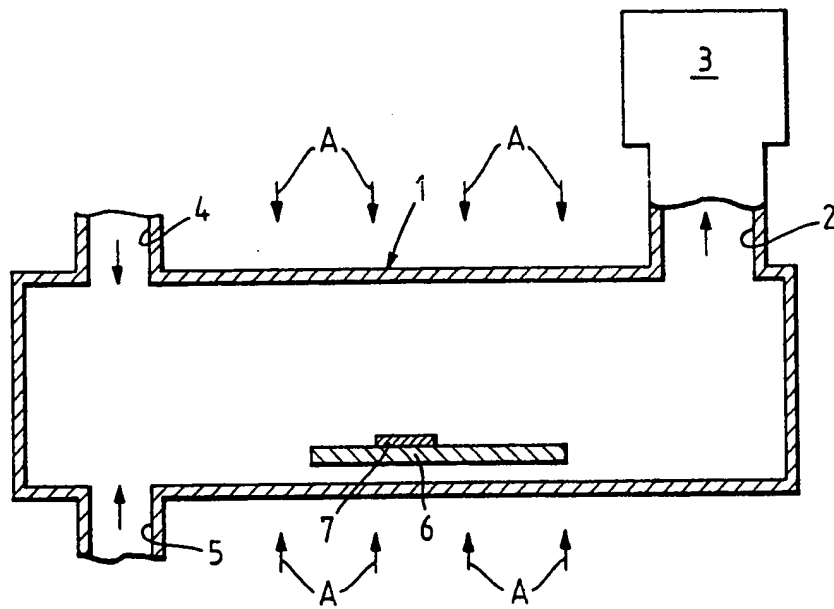


Fig.2.

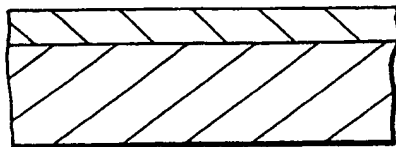


Fig. 3.

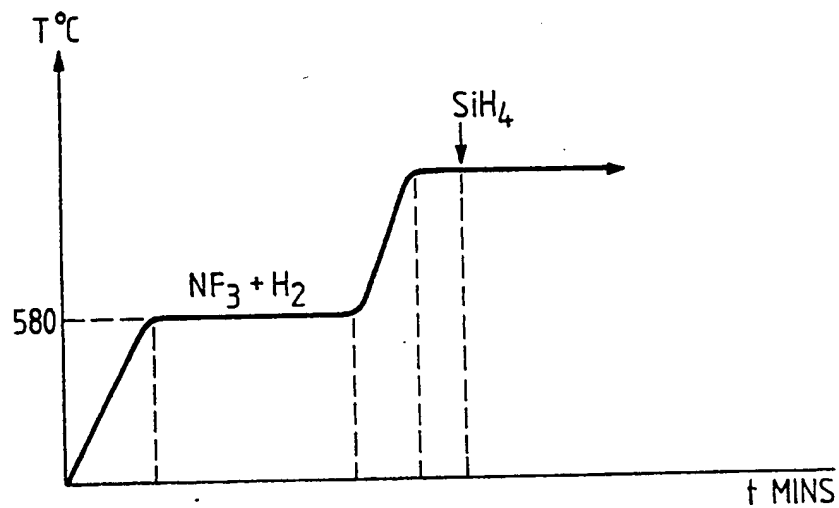
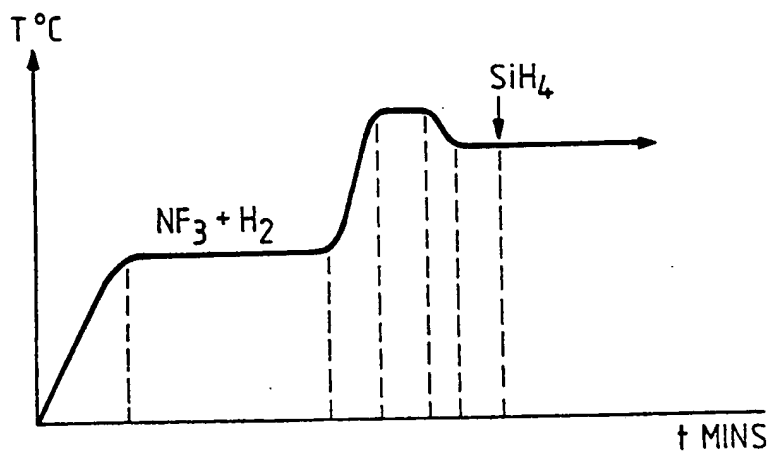


Fig. 4.



DESCRIPTION

A METHOD OF FORMING AN EPITAXIAL LAYER OF SILICON

This invention relates to a method of forming an epitaxial layer of silicon on a surface of a monocrystalline silicon body, which method comprises passing a stream of hydrogen gas over the body, cleaning the surface of the body and passing a silicon-containing gas over the body to commence growth of the epitaxial layer.

GB-A-1071412 describes such a method. In the arrangement described in GB-A-1071412, the surface of the silicon body is cleaned by heating the silicon body to a temperature of 1000 degrees Celsius and passing hydrogen over the body for a period of thirteen minutes with the body maintained at the temperature of 1000 degrees Celsius. After purging of a mixing chamber, the temperature of the body is raised to 1200 degrees Celsius and hydrogen from the supply mixed in the mixing chamber with silicon tetrachloride is passed over the body. The body is maintained at 1200 degrees Celsius for a period of one minute during which silicon produced by reduction of the silicon tetrachloride by the hydrogen is deposited on the body. The temperature of the silicon body is then reduced to 950 degrees Celsius and deposition continued for a further fifteen minutes.

The method described in GB-A-1071412 requires the precleaning of the silicon body in hydrogen at a temperature of 1000 degrees Celsius for thirteen minutes. The silicon body is thus subjected to a high temperature for a relatively long period of time during which problems such as diffusion and/or outgassing may occur in the silicon body.

According to the present invention, there is provided a method of forming an epitaxial layer of silicon on a surface of a monocrystalline silicon body, which method comprises passing a stream of hydrogen gas over the body, cleaning the surface of the body and passing a silicon-containing gas over the body to commence growth of the epitaxial layer, characterised in that the surface of the body is cleaned by, prior to passing the silicon-containing gas

over the body, passing a fluorine-containing gas over the body with the stream of hydrogen gas and in that the body is then heated to the temperature at which the epitaxial layer is to be grown.

5 In a method embodying the invention, the fluorine-containing gas combines with the hydrogen to enable cleaning of the surface of the silicon body at relatively low temperatures, for example below 600 degrees Celsius, and also facilitates the growth of the epitaxial layer at relatively low temperatures, for example at from about 750 degrees Celsius to 900 degrees Celsius. Thus, the problems such as outgassing and/or diffusion of dopants and
10 contaminant species which may occur when high temperature cleaning is used can be reduced.

The fluorine-containing gas may, for example, comprise nitrogen trifluoride. However, other fluorine-containing compounds
15 may be used to provide the fluorine-containing gas, for example hydrogen fluoride, fluorine, xenon difluoride or ClF_3 could be used. These materials are, however, more difficult and/or dangerous to handle than nitrogen trifluoride. Normally, only trace amounts of the fluorine-containing gas are required and thus the
20 fluorine-containing gas may be provided in an inert carrier gas such as argon.

In a preferred method embodying the invention, the fluorine-containing gas is provided by an argon gas supply containing about or less than about 1000 ppm (parts per million) of
25 nitrogen trifluoride and the silicon body is at a temperature of about 580 degrees Celsius during the cleaning which may last about thirty minutes. After the cleaning, the supply of the fluorine-containing gas is switched off, the temperature raised to about 800 or 850 degrees Celsius and the silicon-containing gas, in this
30 example silane, introduced to commence epitaxial growth. The duration for which the silane is introduced will depend upon the desired thickness of the epitaxial layer but the flow rate for the silane may be selected to provide an epitaxial layer growth rate of about 1.7 micrometres per hour. In an alternative arrangement, the
35 temperature may be reduced slightly, from about 850 degrees Celsius

or 800 degrees Celsius to, for example, 750 degrees Celsius prior to introduction of the silane to commence growth of the epitaxial layer.

5 An epitaxial layer grown using a method in accordance with the invention may be used in the manufacture of semiconductor devices where an epitaxial layer is, as would be appreciated by the person skilled in the art, desirable, for example where relatively lowly doped high resistance epitaxial material is desired for achieving high breakdown voltages in power semiconductor devices or in
10 integrated circuits, for example where buried layers are required.

Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings, in which:-

Figure 1 is a simplified schematic partial cross-sectional view of apparatus for carrying out a method embodying the
15 invention;

Figure 2 shows schematically and in cross-section an epitaxial layer of silicon formed on a monocrystalline silicon substrate;

Figure 3 is a schematic graph of change of temperature with time for illustrating a first embodiment of a method in accordance
20 with the invention; and

Figure 4 is a schematic graph of change of temperature with time for illustrating a second embodiment of a method in accordance with the invention.

It should, of course, be understood that the Figures are
25 merely schematic and are not to scale, various relative dimensions having been exaggerated or diminished in the interests of clarity and for ease of understanding.

Referring now to the drawings, Figure 1 shows in a very schematic and simplified form the reaction chamber 1 of chemical
30 vapour deposition apparatus suitable for use in carrying out a method embodying the invention. Any suitable conventional chemical vapour deposition apparatus may be used, for example, the AMC 7810 chemical vapour deposition apparatus manufactured by Applied
Materials Inc. of Santa Clara, California, U.S.A.

35 As illustrated schematically in Figure 1, the reaction chamber

1, which is normally a quartz vessel, has an outlet 3 connecting with a pump 3 of a conventional type for maintaining a desired low pressure, for example in the region of from 0.27 Torr (36 Pa) to 80 Torr (10.7×10^3 Pa), within the reaction chamber 1. As shown, the reaction chamber 1 has two inlets 4 and 5. The first inlet 4 is arranged to be connected via an appropriate valve or switching system (not shown) to separate supplies of hydrogen, nitrogen and a silicon-containing gas such as silane (SiH_4) or trichlorosilane (SiHCl_3) whilst the second inlet 5 is arranged to be connected via an appropriate valve or switching system (not shown) to a supply of an inert carrier gas carrying a trace amount of a fluorine-containing gas. In this example, the inert carrier gas is argon (Ar) carrying about 1000 ppm (parts per million) or less of the fluorine-containing gas which may be nitrogen trifluoride (NF_3).

A graphite susceptor 6 previously coated with, for example, silicon carbide and then polycrystalline silicon to avoid carbon contamination, is used to support a monocrystalline silicon body or substrate 7 within the reaction chamber 1. Alternatively, a silicon susceptor coated with CVD (chemical vapour deposited) polycrystalline silicon may be used. Normally, the susceptor 6 will support a number of substrates 7 although only one is shown in Figure 1.

The arrows A in Figure 1 represent schematically a radiant heating system which is provided around the outside of the reaction chamber 1 for enabling heating of the substrate 7.

Referring now to Figures 1 and 2, a method embodying the invention for forming an epitaxial layer 8 of silicon on a surface 7a of a monocrystalline silicon body or substrate 7 comprises passing a stream of hydrogen gas over the body 7, cleaning the surface 7a of the body 7 and passing a silicon-containing gas over the body 7 to commence growth of the epitaxial layer 8.

In accordance with the invention, the surface 7a of the body 7 is cleaned by, prior to passing the silicon-containing gas, for example silane, over the body, passing a fluorine-containing gas,

for example nitrogen trifluoride carried by an inert carrier gas such as argon, over the body with the body at a temperature, for example below 600 degrees Celsius, below that at which the epitaxial layer is to be formed but at above the temperature at which the fluorine-containing gas decomposes so that the fluorine-containing gas combines with the hydrogen being passed over the body to clean the surface 7a of the body 7. The body 7 is then heated to the temperature at which the epitaxial layer 8 is to be grown, for example from 750 degrees Celsius to 900 degrees Celsius.

A first embodiment of a method in accordance with the invention will now be described in greater detail with reference to Figures 1 and 2 and to Figure 3 which illustrates schematically changes in temperature with time during the carrying out of the method.

Thus initially a monocrystalline silicon substrate 7 which may have a diameter of, for example, 0.05m and an arsenic concentration of, for example, about 2.4×10^{25} atoms m^{-3} is cleaned of surface contaminants and protective thick oxide using a wet chemical cleaning process. The wet chemical cleaning process may consist simply of a hydrofluoric acid dip etch or may be a hydrogen peroxide cleaning process such as described in a paper entitled 'cleaning solutions based on hydrogen peroxide for use in silicon semiconductor technology' by W. Kern and D.A. Puotinen published in the RCA Review June 1970 at pages 187 to 206. Such wet chemical cleaning results in a thin native oxide being present on the surface 7a. This thin native oxide serves to protect the surface 7a from contaminants but, of course, needs to be removed to enable epitaxial growth on the surface 7a.

After the wet chemical cleaning process, the substrate 7 is placed on the susceptor 6 within the reaction chamber 1. The reaction chamber 1 is then, as is conventional in the art, purged with nitrogen and the pressure in the reaction chamber 1 reduced to the desired operating pressure using the pump 3. In this example, the desired operating pressure lies in the range given

above and may be, for example, 1 Torr (133 Pa).

After backfilling and purging of the reaction chamber 1 with hydrogen supplied via the first inlet 4, the substrate 7 is heated, using the radiant heating system surrounding the reaction chamber 1 and indicated schematically in Figure 1 by the arrows A, to a cleaning temperature below that at which epitaxial cleaning temperature below that at which epitaxial growth of silicon is to take place but above that at which the fluorine-containing gas to be supplied via the inlet 5 decomposes. In this example, where the fluorine-containing gas is to be nitrogen trifluoride, the cleaning temperature is, for example, 580 degrees Celsius although it may be possible to use lower temperatures as nitrogen trifluoride decomposes at about 200 degrees Celsius.

Once the substrate 7 has reached the desired cleaning temperature, as indicated at point A in Figure 3, the inert carrier gas providing the fluorine-containing gas is supplied via the second inlet 5. In this example, approximately equal flow rates are used for hydrogen and the inert carrier gas providing the fluorine-containing gas. The hydrogen which should be ultra-pure, for example 99.9999 per cent pure hydrogen supplied via a palladium diffuser as is known in the art, to avoid contamination with, for example, water vapour, may be supplied at a flow rate in the region of from 250 to 500 (cc) centilitres per minute, for example 300 centilitres per minute whilst the inert gas carrying the fluorine-containing gas may be provided with a flow rate of 350 cc per minute.

Only a trace amount of the fluorine-containing gas is required and, in this example, the fluorine-containing gas is supplied as nitrogen trifluoride (NF_3) with a concentration of up to about 1000 ppm (parts per million) in the inert carrier gas which is in this example argon. The inert carrier gas is only provided to give a measurable quantity of gas so that the nitrogen trifluoride concentration can be determined and so could be omitted if desired.

With an external radiant heating system as indicated by the

arrows A in Figure 1 or any other suitable conventional local heating means, the reaction chamber 1 should remain relatively cool except in the vicinity of the susceptor 6. As indicated above, nitrogen trifluoride is stable up to about 200 degrees Celsius and so should only decompose in the vicinity of the heated substrate 7 and there combine with the hydrogen to etch away the native oxide. The exact etching mechanism is not however clear. However, once in the reaction chamber 1 the nitrogen trifluoride either combines in the gas phase with the hydrogen to form hydrogen fluoride or combines with the hydrogen at the heated surface 7a of the substrate 7. In addition, the presence of water molecules in the native oxide, as will normally be the case especially where a wet chemical precleaning treatment has been carried out as described above, may facilitate the etching process.

The cleaning step using the fluorine-containing gas is continued for a time t_1 , which in this example is 30 minutes, although the cleaning step could be shorter. At the end of the desired cleaning time t_1 , that is when the native oxide has been removed, the supply of the inert carrier gas providing the fluorine-containing gas is switched off (point B in Figure 3) and the temperature of the substrate 7 raised using the radiant heating system to the desired epitaxial growth temperature which may be, in this example, 800 or 850 degrees Celsius, 850 degrees Celsius as shown at point C in Figure 3, and allowed to stabilise for a short time period t_2 , in this example two minutes. The appropriate valve or switching system is then activated at point D in Figure 3 to supply the silicon-containing gas, in this example silane (SiH_4). In this example, the flow rate of the hydrogen gas is maintained at 300 cc per minute and a flow rate of 5cc per minute is used for the silane with a partial pressure of 0.01 Torr (1.33 Pa) of silane providing a growth rate of about 1.7 micrometres per hour of epitaxial silicon. It will, of course, be appreciated that the flow of silane will be maintained for a period determined by the desired thickness of the epitaxial layer 8 (Figure 2). In this particular example, the flow of silane is maintained for a period of about 30

minutes so providing an epitaxial layer 8 with a thickness of about 0.9 micrometres.

Figure 4 illustrates graphically the changes in temperature with time during a second embodiment of a method in accordance with the invention.

In the example illustrated by Figure 4, the cleaning step using the fluorine-containing gas is carried out as described above with reference to Figure 3. At the end of the cleaning step (point B in Figure 4), however, the substrate temperature is raised to 800 degrees Celsius (point E in Figure 4) for a short period t_3 , in this example about 10 minutes, and is then allowed to drop to a desired growth temperature of 750 degrees Celsius (point F in Figure 4). The temperature of the substrate is then allowed to stabilise for a short period t_4 , in this example about two minutes, and then the silicon-containing gas, again silane, is introduced (point G in Figure 4). A similar flow rate as described above with reference to Figure 3 may be used for the silane so providing a growth rate for the epitaxial layer 8 of about 1.7 micrometres per hour.

Electron channelling pattern analysis of the layers 8 grown using the methods described above showed the layers 8 to be epitaxial with the substrates 7. Secondary ion mass spectrometry (SIMS) depth profiling of the grown layers and underlying substrates 7 were carried out on each sample to determine the dopant gradient at the interface between the substrate 7 and the epitaxial layer 8 and the dopant gradient at the interface was found to be much sharper than could be resolved by the SIMS analysis technique, the SIMS analysis technique being capable of resolving 8 nanometres per decade change in dopant concentration.

It has also been found that similar results, that is good epitaxial layers 8 with little out-diffusion from the substrate 7 can be obtained without without any wet chemical cleaning of the substrate surface 7a prior to placing the substrates into the reaction chamber 1. In addition, a method embodying the invention may be carried out using a standard design of chemical vapour

depositing apparatus such as the one mentioned above without the need for an ultra-high vacuum environment and thus without the need for the long pump down times associated with ultra-high vacua.

Although, in the examples described above, nitrogen trifluoride is used as the fluorine-containing gas, other fluorine compounds could be used. Thus, for example, hydrogen fluoride, fluorine, xenon difluoride (XeF_2) or ClF_3 could, for example, be used in place of the nitrogen fluoride. These materials are however more difficult or more dangerous to handle than nitrogen trifluoride. In addition, although in the embodiments described above, the silicon-containing gas is not introduced until after the cleaning step has finished, it may be possible to continue the cleaning step with the fluorine containing gas during the deposition or growth of the epitaxial silicon layer 8, especially where one of the other fluorine-containing compounds mentioned above is used.

Although in the methods described above, radiantly heated chemical vapour deposition apparatus is used, apparatus using other forms of heating may be used. Thus, for example, chemical vapour deposition apparatus using a resistive heating system and having a reaction chamber or vessel formed of silicon carbide or silicon may be used.

Epitaxial growth of silicon is an expensive process because in conventional methods, the gas flow needs to be parallel to the surface of the substrate to achieve an even epitaxial growth rate over the whole surface. It has however been found that, using a method embodying the invention, the substrates or wafers can be stacked vertically in the reaction chamber (for example, the silicon carbide or silicon reaction chamber of a resistively heated chemical vapour deposition apparatus), that is perpendicular to the gas flow direction, with a reasonably even growth rate over the substrate surfaces even though the method has not yet been optimised for this configuration. Accordingly, the use of a method embodying the invention should enable cost savings by allowing the wafers or substrates to be stacked vertically rather than horizontally in the reaction chamber.

From reading the present disclosure, other modifications will be apparent to persons skilled in the art. Such modifications may involve other features which are already known in the art and which may be used instead of or in addition to features already described herein. Although claims have been formulated in this application to particular combinations of features, it should be understood that the scope of the disclosure of the present application also includes any novel feature or novel combination of features disclosed herein either explicitly or implicitly or any generalisation or modification of one or more of those features, whether or not it relates to the same invention as presently claimed in any claim and whether or not it mitigates any or all of the same technical problems as does the present invention. The applicants hereby give notice that new claims to such features and/or combinations of such features may be formulated during the prosecution of the present application or of any further application derived therefrom.

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CLAIMS

1. A method of forming an epitaxial layer of silicon on a surface of a monocrystalline silicon body, which method comprises passing a stream of hydrogen gas over the body, cleaning the surface of the body and passing a silicon-containing gas over the body to commence growth of the epitaxial layer, characterised in that the surface of the body is cleaned by, prior to passing the silicon-containing gas over the body, passing a fluorine-containing gas over the body with the stream of hydrogen gas and in that the body is then heated to the temperature at which the epitaxial layer is to be grown.

2. A method according to Claim 1, characterised in that the fluorine-containing gas is provided in an inert carrier gas which contains trace amounts of the fluorine-containing gas.

3. A method according to Claim 2, characterised in that the inert carrier gas is argon containing up to 1000 parts per million of the fluorine-containing gas.

4. A method according to any one of the preceding claims, characterised in that the fluorine-containing gas comprises nitrogen trifluoride.

5. A method according to any one of the preceding claims, characterised in that the body is at a temperature of about 580 degrees Celsius during the passing over the body of the fluorine-containing gas.

6. A method according to any one of the preceding claims, characterised in that the body is heated to a temperature of from about 750 degrees Celsius to about 900 degrees Celsius for growth of the epitaxial layer.

7. A method according to any one of Claims 1 to 5, characterised in that the silicon-containing gas is silane.

8. A method of forming an epitaxial layer of silicon on a surface of a semiconductor body, substantially as hereinbefore described with reference to the accompanying drawings.

9. Any novel feature or combination of features described herein.